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The Isotopic Shift in the Spectrum of Plutonium

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The isotopic shift of 19 lines of plutonium has been found in the region of 4100-6500 Å. It appears that 13 of these lines possess a purely isotopic structure while 6 lines display an isotopic and hyperfine structure. All the lines, with the exception of 6192.63 Å, experience a negative shift. The magnitude of the isotopic shift for the lines measured varies from 0.08 to 0.29 cm^{-1}. On the basis of the data on the isotopic shift and on the hyperfine splitting of the lines, transition schemes for the lines are determined which are based on the hyperfine structure, on the isotopic structure, or on both together. In addition the electronic configurations are predicted for several of the levels, with varying certainty.

I. INTRODUCTION

AT this time much attention is being paid to the investigations of the isotopic shift in the spectrum of elements in the actinium series. The most thoroughly studied isotopic shift is in the spectrum of uranium. Initially this effect was found in the spectrum of uranium by Anderson and White[1] It was then thoroughly investigated in several other researches[2]. Recently the isotopic shift in the spectrum of thorium has been found and studied[3].

While our work was in progress, there appeared a paper on the isotopic shift in the spectrum of plutonium[4]. The authors photographed the spectrum of two-isotope samples of plutonium ($Pu^{238} + Pu^{242}$ and $Pu^{239} + Pu^{240}$) on a large 9-meter diffraction spectrograph (dispersion = 0.92 Å/mm) and they studied the ultraviolet region of the spectra in the interval 3350-4050 Å. Twenty lines were found with a noticeable isotope shift between the Pu^{238} and Pu^{240} components. Of these only four lines were found to have a measurable shift between the Pu^{239} and Pu^{240} components. The resolving power of the set-up above was approximately six times less than the resolving power of our equipment. For this reason the authors[4] were unable to find the hyperfine structure of the lines of the isotope Pu^{239}, which, of course, affected the accuracy of the measurement of the magnitude of the isotopic shift in several cases.

This work, performed in the middle of 1953, is concerned with the investigation of the isotopic shift in the spectrum of plutonium. The problem included the measurement of the intervals between the components of the isotopic structure and the determination of the relation of the intensities of the components of the isotopic structure.

II. EXPERIMENTAL PART

The same kind of discharge tube with hollow cathode and the same kind of vacuum system was used for the excitation of the spectrum of plutonium as had been used by us for the investigation of the hyperfine structure of the lines of U^{233} and Pu^{239} [5]. For an arrangement of high resolving power, a Fabry-Perot etalon was used together with a three-glass prism Steinheil spectrograph. The Fabry-Perot etalon was placed between the source of the light and the spectrograph aperture. The interference picture was projected on the spectrograph slit by means of a Tessar objective ($f = 600$ mm).

For the investigation of the isotopic structure of the spectrum of plutonium a mixture of two isotopes $Pu^{239} + Pu^{240}$, in the form of an oxide, was used. A sample of approximately 8 mg was placed in the (discharge) tube. The plutonium oxide reduced to the metal hydride under electric discharge[5]. The excitation took place under an

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[1] O. E. Anderson, H. K. White, Phys. Rev. 71, 911 (1947)

[2] L. E. Burchart, G. L. Stukenbrocker and S. Adams, Phys. Rev. 75, 83 (1949); J. R. McNally, J. Opt. Soc. Am. 39, 271 (1949); D. D. Smith, G. L. Stukenbrocker and J. R. McNally, Phys. Rev. **84**, 383 (1951)

[3] G. L. Stukenbroker and J. R. McNally, J. Opt. Soc. Am. **43**, 36 (1953)

[4] J. G. Conway and M. Fred, J. Opt. Soc. Am. **43**, 216 (1953)

[5] L. A. Korostyleva, A. R. Striganov and N. M. Iashin, J. Exper. Theoret. Phys. USSR **28**, 471 (1955), Soviet Phys. 1, 310 (1955)

argon pressure of 1-2 mm of mercury and a discharge current of 0.2 amp. Two spectra were photographed in the region 4100-6500 Å with an exposure time of 60 minutes and with intervals of 10 and 15 mm between the plates of the etalon.

III. RESULTS

Having looked carefully at the obtained spectrograms, we have found about twenty lines showing evidence of isotopic structure. Some of the lines found by us were composed of two components, others of three components. Visually comparing the structure of these lines on the spectrograms from the two-isotope sample $Pu^{239} + Pu^{240}$ with the structure of the same lines on the spectrograms from the one-isotope sample Pu^{239}, we have determined that one of the components in the structure of these lines is due to the isotope Pu^{240}. Figure 1 shows as an example the schematic structure of two lines 4493.67 and 4206.37 Å, one of which consists of two components, while the other consists of three (on this and on the following drawings the isotopic components are identified by the mass number). We measured the intensities of the components of a series of spectral lines having isotopic structure. This confirmed the existence of isotopic shift in the spectrum of plutonium.

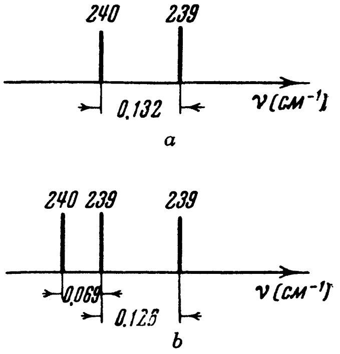

Fig. 1. The structure of the plutonium lines: *a*. $\lambda = 4493.67$ Å: *b*. $\lambda = 4206.37$ Å.

We found 13 lines of plutonium exhibiting a purely isotopic structure and 6 lines with isotopic and hyperfine structure in the region of the spectrum investigated. All lines, with the exception of line 6192.63 Å, were found to have a negative shift (i.e., the component of Pu^{240} is displaced in the direction of lower wave numbers).

Off-center approximations were used to determine the magnitudes of the shifts. The method of Mac Nair[6] was employed in processing the results of the measurements. The final results are shown in Table I. Columns 3 and 4 show the magnitude of the splitting between the Pu^{239} components, column 5 gives the interval between the Pu^{240} component and the neighboring Pu^{239} component. Columns 6 and 7 show the magnitude of the isotopic shift between the Pu^{239} and Pu^{240} components, where for those lines with isotopic and hyperfine structure it was calculated by adding to the interval between the Pu^{239} component and the neighboring Pu^{240} component half the width of the hyperfine structure (columns 3 and 4), without center of mass calculation. The results obtained show that the magnitude of the isotopic shift in the spectrum of plutonium varies between 0.08 and 0.29 cm⁻¹ for a mass number difference, ΔA, between two isotopes equal to 1. The largest shifts are observed for the lines 4159.87; 4396.31; 4468.48; 4484.20; and 4986.72 Å ; the smallest for lines 4567.45; 5590.51; and 6192.63 Å. It is possible to say with certainty that the lines 4393.87, 4441.57, 4491.61 and 4504.80 Å do not exhibit isotopic structure because these lines are not reduced in their intensities in our spectra by comparison with other lines where the Pu^{240} component is found.

The isotopic shift in the spectrum of plutonium is nearly the magnitude of the shifts in the spectra of uranium[2] and thorium[3]. If the isotopic shift in the spectra of the elements of the actinium shell is compared with the isotopic shift of the heavy elements of the preceding shell (Hg, Tl, Pb) it is easily seen that in the region of the actinium shell nuclei there is a "jump" in the value of the isotopic shift. Such "jumps" have already been observed in the cases of cerium, neodymium, samarium and europium, and also in the case of lead. It has been shown over the past few years that these jumps are related to a large deformation of the shape of the nucleus. It is apparently possible in this way to explain the large negative isotopic shift in the spectra of the elements of the actinium series.

IV. ON THE QUESTION OF THE ELECTRONIC CONFIGURATIONS IN THE PLUTONIUM ATOM

All the plutonium lines whose structure we have

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[6] W. A. McNair, Phil. Mag. 2, 613 (1926); S. Tolansky, *High Resolution Spectroscopy*, London, 1947

TABLE I

Spectral lines of plutonium exhibiting isotopic structure.

Wavelength in Å	Intensity	Width of the Hyperfine Structure		Interval between Pu^{240} and neighboring Pu^{239} component in cm	Isotopic shift Pu^{239} - Pu^{240}	
		in cm^{-1}	in Å		in cm^{-1}	in Å
4140.10	3	—	—		—0.197	—0.034
4151.38	4	—	—		—0.167	—0.029
4159.87	4	—	—		—0.261	—0.045
4206.37	7	0.128	0.023	0.069	—0.133	—0.023
4396.31	8	0.09	0.017	0.244	—0.289	—0.058
4468.48	4	0.161	0.032	0.172	—0.252	—0.050
4472.70	10	0.167	0.033	0.075	—0.158	—0.032
4478.63	1	—	—	—	—0.093	—0.019
4484.20	1	—	—	—	—0.239	—0.048
4493.67	10	—	—	—	—0.132	—0.027
4506.56	—	—	—	—	—0.195	—0.040
4567.28	1	—	—	—	—0.111	—0.023
4676.18	1	0.092	0.020	0.177	—0.223	—0.049
4798.93	1	—	—	—	—0.169	—0.039
4986.72	3	—	—	—	—0.235	—0.058
5044.53	2	—	—	—	—0.215	—0.055
5590.51	4	—	—	—	—0.122	—0.038
5630.48	6	—	—	—	—0.123	—0.039
6192.63	7	0.039	0.015	0.058	+0.077	+0.029

investigated can be sorted into four groups.

1. Lines which exhibit only hyperfine structure (in all 65 lines)[5].
2. Lines which undergo a purely isotopic shift (13 lines).
3. Lines which exhibit both hyperfine and isotopic structure (6 lines).
4. Lines which do not undergo either hyperfine splitting or an isotopic shift.

Comparing PuI with SmI, by analogy with UI and NdI, it is thought that the ground state of the neutral atom of plutonium is related to the ground-state configuration $5f^5 6d 7s^2$. In comparison with the classification of the uranium spectra, it is supposed that higher excited states belong to the configurations $5f^5 6d^2 7s$, $5f^5 6d 7s 7p$, $5f^5 7s^2 7p$, $5f^2 6d^2 7p$, $5f^5 6d^3$. In the case of a singly ionized plutonium atom there appear to be two systems of energy levels. Levels of the configurations $5f^5 7s^2$, $5f^5 6d 7s$, $5f^5 6d^2$, $5f^5 7s 7p$, $5f^5 6d 7p$ belong to one of these, while $5f^6 7s$, $5f^6 6d$, $5f^6 7p$ belong to the other.

On the basis of our experimental data it is not difficult to present certain considerations on the electronic configurations to which the levels from several transitions apparently belong. As is known, the energy levels of atoms, having closed shell electronic configurations s^2 and p^6, do not exhibit hyperfine splitting. The largest splitting is experienced by levels related to configurations with one unbalanced s-electron. As far as isotopic shift is concerned, it is strongest for those levels which belong to configurations having a group of penetrating s^2-electrons.

From this it is thought that lines of the first group, which exhibit only hyperfine structure, belong to transitions between levels of the excited configurations of the type $5f^5 6d^2 7p$ - $5f^5 6d^2 7s$ (PuI) or $5f^5 6d 7p$ - $5f^5 6d 7s$ (PuII). One of these levels undergoes doublet splitting. Lines of this group cannot be related to transitions to the ground state with non-excited configurations $5f^5 6d 7s^2$ or $5f^5 7s^2$, since they would then exhibit an isotopic shift.

Lines of the second group, which undergo only an isotopic shift, appear to belong to transitions of the type $5f^5 6d^2 7p$ - $5f^5 6d 7s^2$ (PuI) or $5f^5 6d 7p$ - $5f^5 7s^2$ (PuII), which either end or start with mixed levels. The scheme of such a type of transition is shown by us as Fig. 2*a*. This scheme explains the shift of the Pu^{240} component in the structure of the lines on the red side. Fig. 2*b*

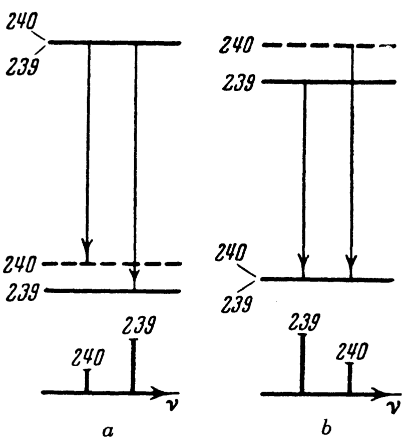

Fig. 2. Transition schemes explaining the isotopic shift:
a. red shift; *b*. violet shift of the component Pu^{240}.

shows a scheme of transitions from upper mixed levels to lower unmixed ones, which corresponds to the shift of the Pu^{240} component in the structure of the lines on the violet side, a type of shift observed on several lines (by Conway and Fred)[4]

Lines of the third group, exhibiting both hyperfine and isotopic structure, seem to be related to transitions of the type $5f^5 6d7s7p$ - $5f^5 6d7s^2$ (PuI) or $5f^5 7s7p$ - $5f^5 7s^2$ (PuII). Levels of these transitions experience at the same time both hyperfine splitting and an isotopic shift. Fig. 3 shows four schemes which permit an explanation of the origin of the observed structure of all six lines belonging to this group. Apparently these lines are related to the transitions between levels of low-excited configurations and levels of non-excited configuration.

Lines of the fourth group are apparently related to transitions between levels of configurations with non-penetrating *f*, *d*, and *p* electrons, and also to highly excited levels of configurations with *s* and s^2-electrons which do not undergo observable hyperfine splitting and isotopic shift.

We see, using the results of the investigations of the hyperfine structure and the isotopic shift in the spectrum of uranium, it is possible to get fairly important information concerning its classification. However the complete interpretation of the spectrum of plutonium is only possible on the basis of an investigation of the Zeeman effect. The data on the hyperfine structure and isotopic shift can be used only as an auxiliary aid in the assignment of levels to a particular electronic configuration. In conclusion, we note that the transition schemes discussed are related to the case of normal order of the isotope terms in accordance with the general

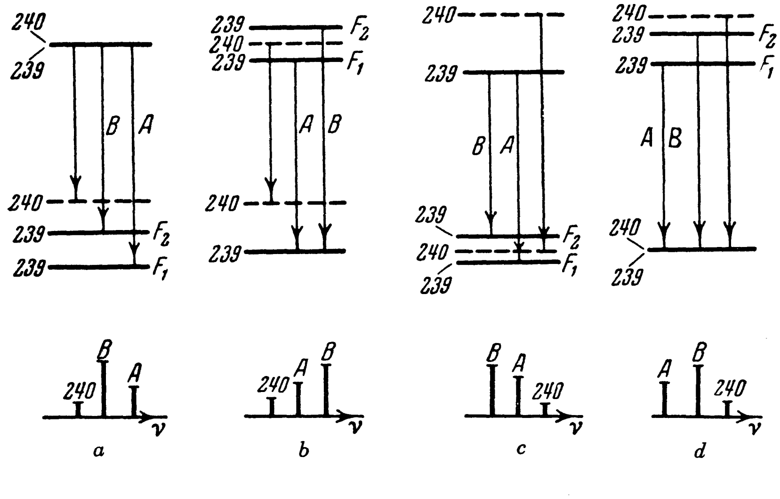

Fig. 3. Schemes of transitions explaining lines of mixed structure.
a and *b*: red shift of the Pu^{240} component with alternate intensities of the components *A* and *B* of the hyperfine structure of isotope Pu^{239}; *c* and *d*: violet shift with alternate intensities of the components *A* and *B* of the hyperfine structure.

theory of the isotopic effect (the terms of the lighter isotopes are placed deeper). One should keep in mind the fact that in complicated atoms non-normal positions of the isotope terms are sometimes found as the results of perturbation.

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The Double Configuration Approximation to the Two Lowest Configurations of the Boron Atom

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The solutions of the equations of the self-consistent field without exchange are presented for the configurations $1s^2 2s^2 2p$ and $1s^2 2s^2 3s$ of boron. The values of the total energy, both in single configuration as well as in the double configuration approximation $1s^2 2s^2 2p^k 3s^{1-k} - 1s^2 2p^{k+2} 3s^{1-k}$ ($k = 1, 0$) are computed with the help of these solutions. With the aid of the solutions of the equation of the self-consistent field without exchange, there are also computed the mass effect, the total dipole strength and the transition probability for the transition $1s^2 2s^2 3s - 1s^2 2s^2 2p$, both in the single configuration and the double configuration approximations.

1. INTRODUCTION

THE present work is devoted to the application of a multiple configuration approximation to the two lowest configurations $1s^2 2s^2 2p$ and $1s^2 2s^2 3s$ of the boron atom with the help of the solution of the equation of the self-consistent field without exchange. The method of analysis carried out in reference 1 shows that while we use single electron wave functions, which are determined in the single configuration approximation, the multiple configuration approximation, in practice, reduces to the double configuration approximation: $1s^2 2s^2 2p^k 3s^{1-k} - 1s^2 2p^{k+2} 3s^{1-k}$, where $k = 1$ or 0.

The approximate solutions for the lowest configuration, which were obtained in reference 2, were used as the initial functions for the solution of the self-consistent field equation without exchange. In both configurations, the solution was carried out to the degree of self-consistency 0.0015 [cf. Eq. (2.8) in reference 3]. The orthonormalized solutions are presented in Table I. The orthonormalization was obtained by means of Eqs. (2.2) and (2.3) of reference 4, and the values of the constants c_{ik} are also given in Table I.

2. NUMERICAL CALCULATION OF THE ENERGY

The non-diagonal matrix element of the energy, which combines the investigated configurations $1s^2 2s^2 2p^k 3s^{1-k}$ with a consideration of the configuration $1s^2 2p^{k+2} 3s^{1-k}$, can be put in the following form:

$$E_{12} = (-1)^{k+1} \frac{\sqrt{3-k}}{3} G_1(2s, 2p)_{12} N^2(1s, 1s)_{12} N^k \times (2p, 2p)_{12} N^{1-k}(3s, 3s)_{12}, \quad k = 1, 0. \quad (1)$$

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[2] F. W. Brown, J. H. Bartlett and C. G. Dunn, Phys. Rev. 44, 296 (1933)

[3] A. P. Iutsis and G. K. Tsiunaitis, J. Exper. Theoret. Phys. USSR 23, 512 (1952)

[4] G. K. Tsiunaitis and A. P. Iutsis, J. Exper. Theoret. Phys. USSR 25, 679 (1953)